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Extended Summary

Pesticide Adsorption as a Function of Depth below Surface*

Gitte Felding

Danish Institute of Plant and Soil Science, Department of Weed Control and Pesticide Ecology, Flakkebjerg, DK-4200 Slagelse, Denmark

Abstract: The adsorption of atrazine and mecoprop to soil at different levels below the surface was measured and compared with values calculated from the partition coefficient—between soil organic carbon and water—and the carbon content. With soil samples from the top layers, the calculated values were in fairly good agreement with the measured values. Below the top layers, the importance of the effect of clay content on the adsorption is reflected in the difference between the measured and calculated K_d values. Calculated values can be unrealistically low resulting in overestimates of leaching.

Key words: adsorption, partition coefficient, K_d, atrazine, mecoprop

Introduction

The adsorption of a pesticide to soil can be expressed as its K_d value which, according to Karickhoff,[1,2] can be calculated from the carbon content in soil (C; %) and the partition coefficient (K_{oc}) for the pesticide:

$$K_{oc} = \frac{K_d \cdot 100}{C}$$

In this study we have measured the carbon content and the K_d values for samples taken from different levels below the soil surface and calculated K_{oc} values for each level. For comparison, K_d values were calculated using the carbon content and the K_{oc} value from the top horizon or a value selected from the Pesticide Properties Database for Environmental Decision-Making;[3] these are referred to as calculated $K_{d\,top}$ and calculated $K_{d\,database}$, respectively.

Experimental

The adsorption of atrazine and mecoprop were determined according to the OECD Test Guideline 'Adsorption-desorption'[4] by shaking sterilised soil (5 g) with calcium chloride solution (0·01 M; 25 ml) containing [^{14}C]atrazine or [^{14}C]mecoprop (5 mg litre^{-1}) for 16 h. The concentration of the herbicide in the aqueous phase was determined in the supernatant after centrifugation, using liquid scintillation counting (LKB 1215).

Studies with atrazine[5,6] were performed at sites at East Zealand (Køge), South Lolland (Bremersvold), Gjellerup and Drengsted, the last two being in South Jutland. Soils at the first two sites were classified as 'clay' soils by Danish criteria but would be regarded as a sandy loam (in the plough layer) or as a sandy clay loam (below the plough layer) if the US Department of Agriculture classification[7] was used. Soil at Gjellerup was classified as a loamy sand loam and that at Drengsted as a loamy sand/sand using the USDA classification.

Studies with mecocrop were conducted at Farre and at Fladerne Bæk and some results from the latter study have been published.[8] The soil at Farre (East Jutland) is a sandy loam and that at Fladerne Bæk (Central Jutland) is a sandy soil according to the USDA classification.

Soil samples were taken at different levels (between 0 and 200 cm) below the surface and their carbon content was determined with a LECO Carbon Analyser.

Results and Discussion

Table 1 lists data for atrazine, which indicate good agreement between measured and calculated K_d values for samples of Bremersvold soil down to 60 cm below the surface, after which the divergence between the experimental and calculated values becomes progressively greater; for samples of Køge soil there is a similar pattern down to 40 cm below the surface. This agreement is most pronounced when the calculated $K_{d\,top}$ value is used. Data in Table 1 from the sandy soils indicate that the difference between the calculated K_{oc} values through the soil profiles was not as big as that with the corresponding values from the clayey soils. Using a K_{oc} value from the mentioned database gave too low K_d values for location Gjellerup.

Table 2 lists data for mecoprop and the Farre and Fladerne Bæk soils. Again, the agreement between measured K_d and calculated ($K_{d\,top}$) values deteriorates with

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TABLE 1
Measured and Calculated Values for the Adsorption of Atrazine to Soil at Different Levels with Two Clayey Soils (Bremersvold and Køge) and Two Sandy Soils (Gjellerup and Drengsted) plus the Carbon Content

Location depth below surface (cm)	*Carbon content* (%)	*Measured* K_d (*ml g*$^{-1}$)	*Calculated*[a] K_{oc} (*ml g*$^{-1}$)	*Calculated*[b] $K_{d\ top}$ (*ml g*$^{-1}$)	*Calculated*[c] $K_{d\ database}$ (*ml g*$^{-1}$)
Bremersvold					
0–20	1·9	1·68	88	1·7	1·9
20–40	1·6	1·08	68	1·4	1·6
40–60	0·4	0·39	98	0·4	0·4
60–80	0·1	0·37	370	0·1	0·1
80–120	<0·05	0·26	>520	<0·04	<0·05
Køge					
0–20	1·3	1·71	132	1·7	1·3
20–40	0·3	0·48	160	0·4	0·3
40–80	0·1	0·42	420	0·1	0·1
80–120	<0·05	0·35	>700	<0·07	<0·05
Gjellerup					
15	1·86	7·4	398	7·4	1·86
50	0·52	1·5	289	2·1	0·52
100	0·12	0·6	500	0·5	0·12
150	0·06	0·3	500	0·2	0·06
200	0·06	0·5	833	0·2	0·06
Drengsted					
15	2·62	5·2	199	5·2	2·62
50	0·64	0·6	54	1·3	0·64
100	0·12	0·1	83	0·2	0·12
130	0·06	0·1	167	0·1	0·06

[a] Calculated from $K_{oc} = K_d \times 100/C$.
[b] Calculated using the K_{oc} value for the top horizon.
[c] Calculated using the K_{oc} value for 100 ml g^{-1} from the Pesticide Properties Database.[3]

increasing soil depth. The difference between measured and calculated K_d value is probably due to two factors:

1. the fact that adsorption was calculated only as a function of carbon content, and

2. the influence of the clay content of the samples, particularly those taken at considerable depths.

Experiments with atrazine at Bremersvold and Køge also examined the effect on adsorption of increasing the

TABLE 2
Measured and Calculated Values for the Adsorption of Mecoprop to Different Levels through a Clayey (Farre) and a Sandy (Fladerne Bæk) Soil Profile

Location depth below surface (cm)	*Carbon content* (%)	*Measured* K_d (*ml g*$^{-1}$)	*Calculated*[a] K_{oc} (*ml g*$^{-1}$)	*Calculated*[b] $K_{d\ top}$ (*ml g*$^{-1}$)	*Calculated*[c] $K_{d\ database}$ (*ml g*$^{-1}$)
Farre					
0–15	2·6	0·56	22	0·56	0·52
40–55	0·3	0·27	90	0·06	0·06
95–105	0·2	0·38	190	0·04	0·04
Fladerne Bæk					
0–30	1·6	0·60	38	0·6	0·3
50	0·5	0·50	100	0·2	0·1
75	0·1	0·27	270	0·04	0·02

[a] Calculated from $K_{oc} = K_d \times 100/C$.
[b] Calculated using the K_{oc} value for the top horizon.
[c] Calculated using the K_{oc} value for 20 ml g^{-1} from the Pesticide Properties Database.[3]

TABLE 3
K_d Values for Atrazine Measured at Bremersvold and Køge in the Horizon 80–120 cm below Surface Using a Range of Concentrations of Atrazine

Atrazine concentration ($\mu g\ litre^{-1}$)	*Bremersvold* K_d ($ml\ g^{-1}$)	*Køge* K_d ($ml\ g^{-1}$)
1·6	0·53	0·60
8·1	0·33	0·40
40·7	0·42	0·20
5000	0·26	0·35

concentration of atrazine with soil samples taken from the layer 80–120 cm below the surface. As the concentration of pesticide below the root zone tends to be lower than that in the plough layer, values of K_d were determined[5] at concentrations considerably below the 5 mg litre^{-1} used in the other experiments. The data in Table 3 indicate a tendency for the adsorption of atrazine to decrease with increasing atrazine concentration.

Conclusion

Calculation of K_d values using the carbon content of the soil and an average K_{oc} value will usually give low values for soil samples taken from below the plough layer because the clay in such samples influences the adsorption of pesticides.

K_d values for soil samples taken from beneath the plough line measured according to the OECD guidelines will often be too low. This is because the inherent pesticide content affects the degree of adsorption and, because such samples are likely to contain less pesticide than those taken from the plough layer, the extent of adsorption of pesticide is likely to be greater than in samples from the plough layer (Table 3).

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